CO_2-in-Water Emulsion Stabilized by Pulverized Limestone for Benign Ocean Storage

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Abstract

When ordinary seawater and liquid carbon dioxide are mixed in the presence of pulverized limestone ($CaCO_3$), a macro-emulsion is formed. The emulsion consists of liquid CO_2 droplets sheathed with a monolayer of calcite crystals dispersed in water. The sheath of crystals prevents the coalescence of the CO_2 droplets. The emulsion has a gross density that is greater than seawater, therefore upon release from a pipe the emulsion plume will sink deeper into the density-stratified ocean while entraining ambient seawater until an equilibrium is reached. After equilibration with the ambient seawater, the individual calcite-sheathed CO_2 droplets ("*globules*") will "rain-out" from the plume toward the ocean bottom, where eventually they will disintegrate due to wave and sediment action. The settling velocity of the globules was measured in the NETL water tunnel facility.

This mode of CO_2 release may prevent acidification of the seawater around the injection point, which is a major environmental drawback of ocean storage of CO_2. Also, the injection can occur at a relatively shallow depth of about 500 m, which saves transportation cost compared to intermediate (1000 – 1500 m) or very deep (> 3000 m) releases suggested by other authors.

Introduction

The major drawback of deep ocean storage of CO_2 is that seawater around the injection point becomes acidified due to the formation of carbonic acid. Aquatic organisms may be harmed in an acid medium (Caulfield et al., 1997). Therefore, a method is described that avoids acidification. Liquid CO_2 is emulsified in water in the presence of finely pulverized $CaCO_3$. The emulsion consists of tiny CO_2 droplets sheathed with a layer of $CaCO_3$ particles dispersed in water. We call the sheathed droplets *globules.* Because of the sheath of $CaCO_3$ around the droplets, and the presence of excess $CaCO_3$, the emulsion is slightly alkaline, not acidic. Furthermore, the emulsion is heavier than seawater, therefore the emulsion plume is expected to sink deeper from the injection point while entraining ambient seawater. Depending on the amount of the injected emulsion, and the exit velocity from the injection pipe, the plume may sink several hundred meters before it equilibrates with the ambient density-stratified seawater (Wannamaker and Adams, 2003). The emulsion may be injected below the depth where liquid CO_2 would flash into vapor, that is, slightly below 500 m, where the hydrostatic pressure is about 5 MPa. This depth may be reached by pipes at relatively short horizontal distances from the coasts of many industrial countries.

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Experimental

Studies of the emulsion formation and its characteristics were performed in a High Pressure Batch Reactor (HPBR) with view windows described by Golomb et al. (2004). The HPBR was transferred and adapted to the DOE/NETL Water Tunnel Facility (WTF) described by Warzinski et al. (2004). The joint HPBR/WTF setup is depicted in Figure 1. The emulsion was created in the HPBR using a slurry of Sigma Corp. reagent grade $CaCO_3$ in de-ionized water mixed about 2:1 by volume with liquid CO_2. The average particle size of $CaCO_3$ is in the 10 – 20 μm range. Under mild mixing conditions, rather large globules were formed, in the 800 – 900 μm range. The resulting emulsion was transferred from the HPBR by pipe into the WTF, where it was stored in a pivoting cup. The cup was slowly rotated, so that the globules spilled into the pressurized water column of the WTF. The descent of individual globules was monitored by video cameras through oblong windows mounted on the WTF.

Results

From the measured descent rate of the globules, and using Stokes' Law for estimating the settling velocity of small spheres through a viscous medium, the globules' density was calculated. Knowing the density of liquid CO_2 at the pressure and temperature conditions of the WTF (930 kg m^{-3}, 15^oC), the thickness of the sheath of $CaCO_3$ particles was calculated that corresponded to the settling velocity of the globules. A particle density of 2700 kg m^{-3} was assumed, which is the listed density of calcite (CRC, 1980). The results are given in Table 1. Four measurements gave an average globule density of 1068.7 kg m^{-3}, and an average $CaCO_3$ sheath thickness of 13 μm. The calculated sheath thickness is in the range of Sigma Corp. $CaCO_3$ particle size, indicating that the CO_2 droplets are sheathed with a monolayer of particles. Figure 2 gives an optical microscope photograph of the globules. The sheath of particles surrounding the globules is clearly visible.The sheath of particles prevents the coalescence of CO_2 droplets into a bulk phase, which would be the case in the absence of particles.

Implication for Ocean Storage of CO_2

When injected from a pipe into the deep ocean, the emulsion will act as a dense plume. Assuming an initial CO_2 : seawater ratio of 1 : 2, and a CO_2 : $CaCO_3$ weight ratio 1 : 0.75 (including some excess $CaCO_3$ for buffering purposes), the initial emulsion density emerging from the pipe is estimated at 1140 kg m^{-3}. Depending on the amount of emulsion injected, the depth of injection, and the density stratification of the ocean, the emulsion plume is expected to descend several hundred meters while entraining ambient seawater (Wannamaker and Adams, 2003). Upon equilibration with the ambient seawater, the individual globules will "rain out" from the plume toward the ocean bottom at a settling velocity of about 0.01 m s^{-1} (Table 1).

Because ocean sequestration will involve large quantities of CO_2 (for example, a 500 MW coal fueled power plant delivers about 100 kg s^{-1} of CO_2), a continuous rather than a batch-type delivery system is more practical. Also, the system should be relatively simple, with minimum cost and energy penalty. Because of the much lower transport cost in a pipeline rather than in a tanker, the focus here is on a pipeline delivery system. Figure 3 depicts a plausible system. Liquid CO_2 captured from a power plant is stored on-shore in a tank. The CO_2 is piped by virtue of gravity with the required assistance of a pump along the continental slope to a static mixer mounted on the slope at a depth of about 500 m. A schematic of a static mixer is given in Figure 4. On-shore, a dense slurry of finely pulverized limestone is prepared (high purity is not required) in seawater in a continuous mixer. The make-up seawater for the slurry is pumped from below the photic zone, so as to minimally disturb aquatic organisms. Because the slurry is denser than seawater, no pumping is required to deliver the slurry to the depth-mounted static mixer. Additional seawater is introduced into the static mixer so as to obtain a CO_2 : seawater volume ratio of approximately 1 : 2. The static mixer emulsifies the feed materials without moving parts and a dense sinking plume of the emulsion is discharged into the ocean.

Conclusion

A system is described that can deliver to the deep ocean (500 m or deeper), an emulsion consisting of tiny CO_2 droplets sheathed with pulverized limestone particles dispersed in seawater. The emulsion plume is expected to sink deeper from the release point because it is denser than ambient seawater. The $CaCO_3$-sheathed globules are expected to rain out from the neutrally buoyant plume toward the ocean bottom. While adding pulverized limestone to liquid CO_2, and employment of the necessary mixing apparatus, will increase the cost of ocean sequestration of CO_2, the added cost may be more than compensated by savings realized by eliminating the need for transporting CO_2 to greater depths. Furthermore, this method of CO_2 sequestration is not expected to acidify the ocean to the same extent as disposal of pure liquid CO_2 would.

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Table I: Globule Density, Diameter and Settling Velocity

	Globule #1	Globule #2	Globule #3	Globule #4	Average of Calculation
Settling Velocity (m/s)	0.012	0.010	0.0099	0.0094	---
Diameter (mm)	0.93	0.86	0.68	0.89	---
Globule Density (kg/m^3)	1065.4	1064.5	1085. 2	1059.7	1068.7
Sheath Thickness (μm)	14.0	12.9	12.3	12.8	13.0

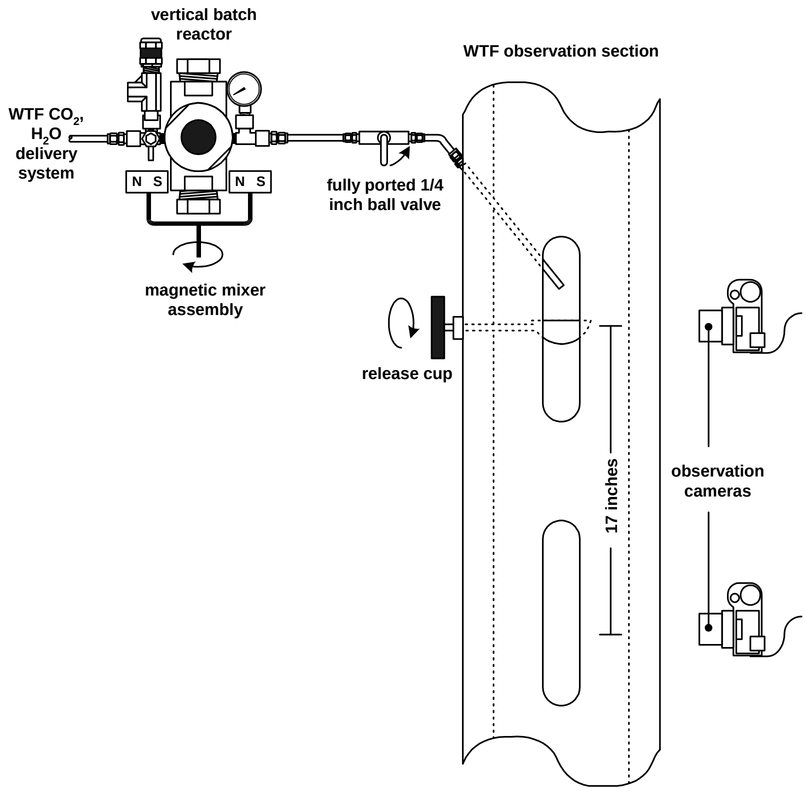

Figure 1. Joint High Pressure Batch Reactor-Water Tunnel Facility Setup

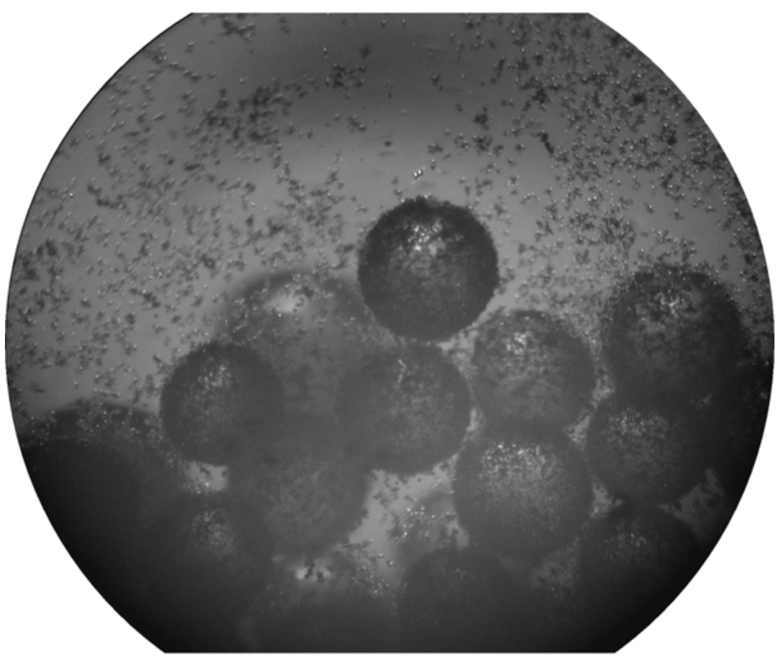

Figure 2. Optical Microscopy of $CaCO_3$-Sheathed CO_2 Globules

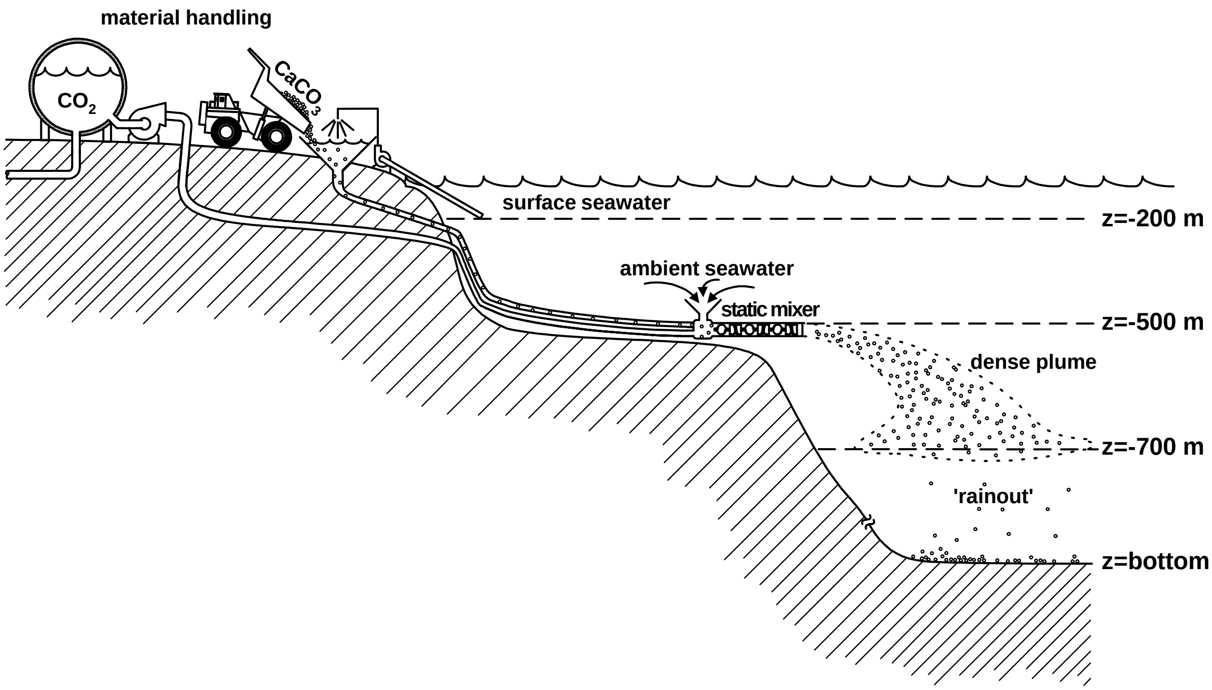

Figure 3. Deep Ocean Delivery System of Emulsion

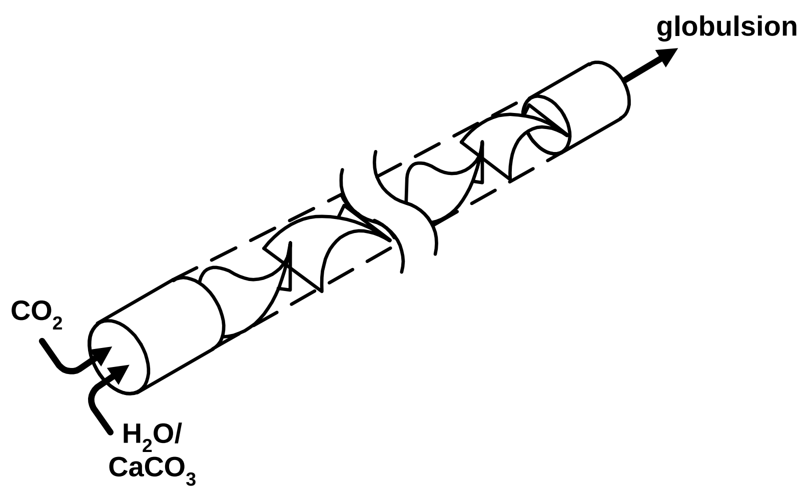

Figure 4. Schematic of Static Mixer